DETERMINATION OF LEAD, CADMIUM AND ANTIMONY CONTENT IN A CERAMIC GLAZE

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ABSTRACT

The presence of heavy metals in tile surface coating has an effect on the surrounding environment and anti-pollution measures has been taken at different levels, one of which consists in using materials with low content in harmful components. In particular Pb, Cd and Sb limits are indicated in Ecolabel, a labelling system for ceramic tiles. This paper describes the validation of method used to determine the percentage of the three oxides in a ceramic glaze because a standard generally accepted procedure does not yet exist. Three commercial glazes samples and one glass certified reference material have been investigated. The dissolution of samples is carried out by acid digestion by heating a known amount of powder with HNO_3 and HF additions. The solution is investigated by Inductively Coupled Plasma Atomic Emission Spectrometry. Detection limit, recovery, repeatability and the uncertainty of measurement were calculated. The results seem to underline that the calculated uncertainty fits the method parameters requested, but the problem is not the compliance with the permissible limits. The fact of the matter is that the limits are so low that the aim of the method is to confirm if the banned elements is present or not in the ceramic glaze.

1. INTRODUCTION

It is common to apply a surface coating to tiles [1], which, when fired, produces a vitreous layer that is hygienic, easily cleanable and provides aesthetic qualities. In selecting raw materials it can generally be stated that the cations having high coordination strengths with respect to the oxygen anion behave as lattice-formers (Si^{4+}, B^{3+}) while those with the lowest values act as lattice modifiers (Pb^{2+}, Ca^{2+}, Ba^{2+}, Na^{+}, K^{+}, Li^{+}) and finally, those have intermediate values may perform both functions (Fe^{3+}, Be^{2+}, Mg^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+}). This presence of heavy metals has an effect on the surrounding environment and anti-pollution measures has been taken at different levels, one of which consists in using materials with low content in harmful components according to Ecolabel [2]. This is a labelling system for consumer products (excluding foods and medicine) that are made in a fashion that avoids detrimental effects on the environment. Just as for the quality assurance labelling systems it is of imperative importance that the labelling entity is clearly divided from and independent of the manufacturers. All ecolabelling is voluntary, meaning that they are not mandatory by law. The EU Ecolabel makes it easier for consumers to choose green products. It is a voluntary scheme designed to encourage businesses to market products and services that are kinder to the environment and for European consumers - including public and private purchasers - to easily identify them. The scheme came into operation with European Agreement CE n°1980/2000 and was designed to identify products which are less harmful to the environment than equivalent brands. The labels are awarded on environmental criteria set by the European Union. These cover the whole life cycle of a product, from the extraction of raw materials, through manufacture, distribution, use and disposal of the product. There are already 26 product groups covering twelve major areas of manufacturing and one service activity. The group of our interest is named: "Hard coverings" according to CE n°272/2002 [3] and CE n°607/2009 [4] and follows the principles according to which: water and energy consumption during manufacturing are limited; residues of dangerous substances for health and the environment are minimized; harmful emissions to air and water are limited; the product includes waste management instructions. In particular Pb, Cd and Sb limits are indicated in Ecolabel and this paper describes the validation [5,6] of method, starting from the existing experience of the chemical laboratory [7,8] to determine the total percentage of the three metals in a ceramic glaze because a standard generally accepted procedure does not yet exist.

2. MATERIALS AND EXPERIMENTAL PROCEDURES

2.1. Samples.

Standard Reference Materials with known content of Pb, Cd and Sb in a ceramic glaze are not available. The analyses are run on a standard reference glass (NBS Standard Reference Material 1412 Multicomponent Glass) called further

"Multicomponent Glass", and three commercial glazes complete with manufacturer chemical analysis. These three samples are marked with the laboratory code: "Glaze C1" - "Glaze C2" - "Glaze C3". The following table 1 shows the percentage values of Pb, Cd and Sb oxides as reported in the respective manufacturer analysis certificates of the 4 sample under investigation. These values are considered the "true value" for all the statistical study concerning this work.

	PbO %	CdO %	Sb_2O_3 %
Multicomponent Glass	4.40	4.38	---
GLAZE C1	---	0.27	0.12
GLAZE C2	0.70	---	---
GLAZE C3	1.50	---	0.88

Table 1. percentage values of Pb, Cd and Sb oxides.

2.2. Reagents [9] and Icp-Oes instrumentation [10,11].

Hydrofluoric acid (39.5% m/v, analytic grade).

Nitric acid (69.5% m/v, analytic grade).

ICP Certified Standard solutions (1000 mg/l) of Pb, Cd and Sb.

Deionized water quality 2 according UNI EN ISO 3696:1996 [12].

The instrumental measurements are performed by Inductively Coupled Plasma Atomic Emission Spectrometry ICP-OES axial view equipped with GemCone nebulizer and a corrosion-resistant Scott-type spray chamber. In table 2 Detection Limit (DL), critical concentration (QL) and Back Equivalent Concentration (BEC) about Pb, Sb and Cd calculated according to UNICHIM GUIDE n° 177/3 [13] are reported.

	DL	Critical Conc	BEC
Pb	0.01 mg/l	0.1 mg/l	0.09 mg/l
Cd	0.0005 mg/l	0.005 mg/l	0.003 mg/l
Sb	0.02 mg/l	0.2 mg/l	0.03 mg/l

Table 2. instrumental parameters.

2.3. Acid digestion procedure.

Samples are dried in oven at 105 ± 5 °C and milled in order to obtain powder under 125 μm (200 ± 5) mg of powder are weighed in platinum crucible, with HNO_3 and HF acid added in excess and warmed on a sand bath. After complete evaporation of the solution the residue is dissolved with HNO_3 1N and put in a 100ml flask of class A [14,15]. The final solution is evaluated via ICP-OES. Starting from certified Pb, Sb and Cd solutions of 1000 mg/l calibration standards are prepared with the following concentrations (table 3):

Element	Standard 1 mg/l	Standard 2 mg/l	Standard 3 mg/l
Lead	3	10	30
Cadmium	0.5	1	3
Antimony	1	3	10

Table 3. Calibration standard concentrations.

The calibration curves, plotted by 4 points (three standards and a blank solution), with correlation coefficient (r) ranging between 0.9990 and 1.0000 are accepted.

The experimental values of the Pb, Sb and Cd amount in the solution are expressed in mg/l. The final results are expressed as oxide percentage of the different elements calculated with the following formula:

$$\%M_xO_y = \frac{C \times V \times 100 \times F}{1000 \times 1000 \times P}$$

where:

C concentration, in mg/l, of lead, cadmium and antimony in solution.

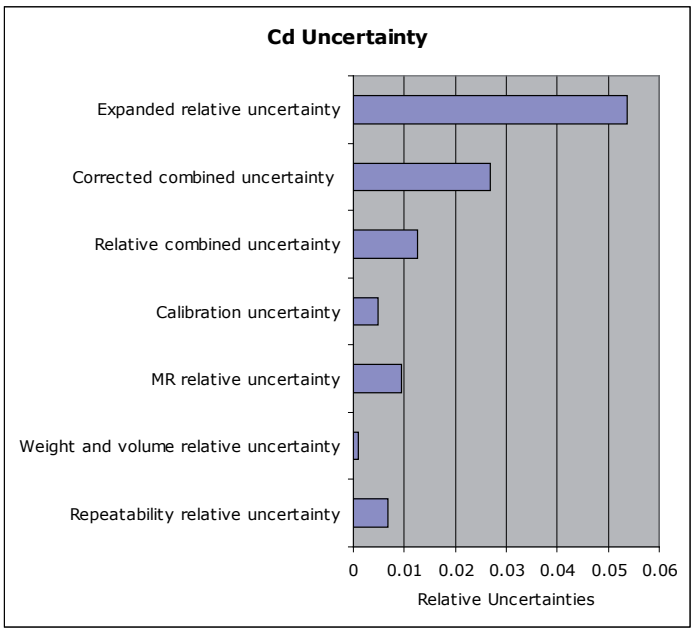
V volume, in ml, of solution.

F stoichiometric factor to proceed from the element to the corresponding oxide.

P Weight, in g, of digested sample.

3. RESULTS

Glaze C1- CdO (0.27±0.01)%

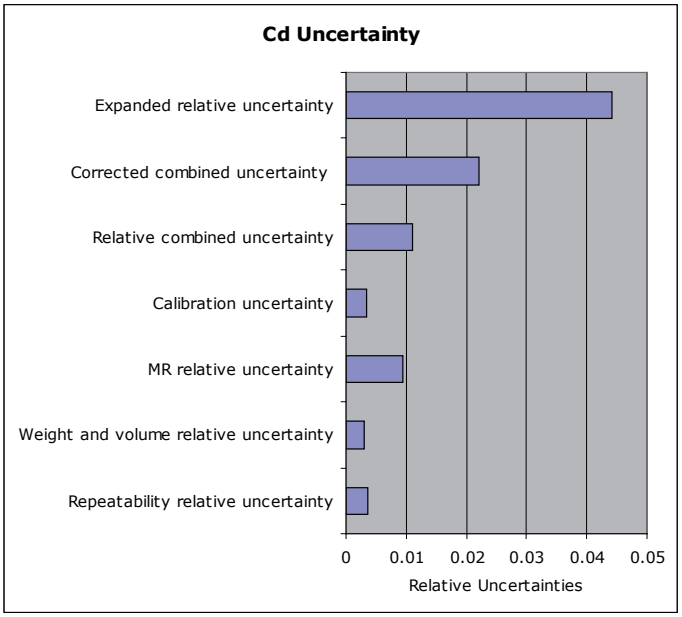


Graph 1. Glaze C1-relative contributions to Cd uncertainty.

Repeatability relative uncertainty	Weight and volume relative uncertainty	MR relative uncertainty	Calibration uncertainty	Relative combined uncertainty	Corrected combined uncertainty	Expanded relative uncertainty	Expanded uncertainty %
0.006874	0.000946	0.009416	0.004821	0.012651	0.026838	0.053676	0.01449

Table 4. Glaze C1-Cd uncertainty contributions.

Reference Material Multicomponent Glass – CdO (4.38± 0.19)%

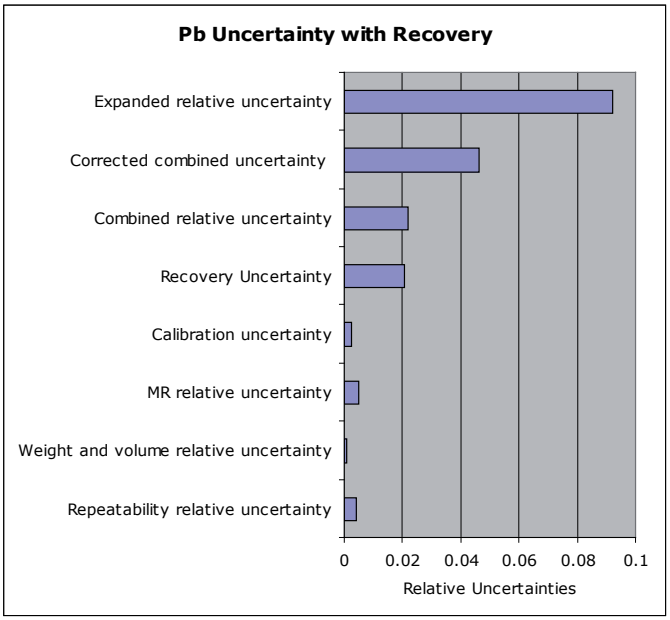


Graph 2. Multicomponent Glass-relative contributions to Cd uncertainty.

Repeatability relative uncertainty	Weight and volume relative uncertainty	MR relative uncertainty	Calibration uncertainty	Relative combined uncertainty	Corrected combined uncertainty	Expanded relative uncertainty	Expanded uncertainty %
0.003583	0.003014	0.009416	0.003326	0.011030	0.022059	0.044119	0.19324

Table 5. Multicomponent Glass –Cd uncertainty contributions.

Glaze C2 - PbO (0.70±0.06)%

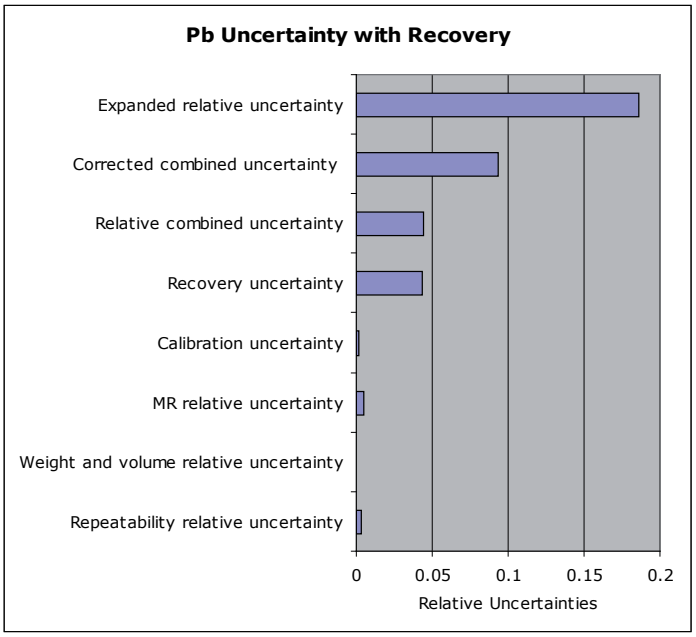


Graph 3. Glaze C2-relative contributions to Pb uncertainty.

Repeatability relative uncertainty	Weight and volume relative uncertainty	MR relative uncertainty	Calibration uncertainty	Recovery uncertainty	Relative combined uncertainty	Corrected combined uncertainty	Expanded relative uncertainty	Expanded uncertainty %
0.004058	0.000946	0.004967	0.002648	0.020611	0.021768	0.046177	0.092353	0.06465

Table 6. Glaze C2–Pb uncertainty contributions.

Glaze C3 – PbO (1.50±0.28)%



Graph 4. Glaze C3-relative contributions to Pb uncertainty.

Repeatability relative uncertainty	Weight and volume relative uncertainty	MR relative uncertainty	Calibration uncertainty	Recovery uncertainty	Relative combined uncertainty	Corrected combined uncertainty	Expanded relative uncertainty	Expanded uncertainty %
0.003254	0.000946	0.004967	0.001385	0.043423	0.043859	0.093040	0.186079	0.27911

Table 7. Glaze C3–Pb uncertainty contributions.

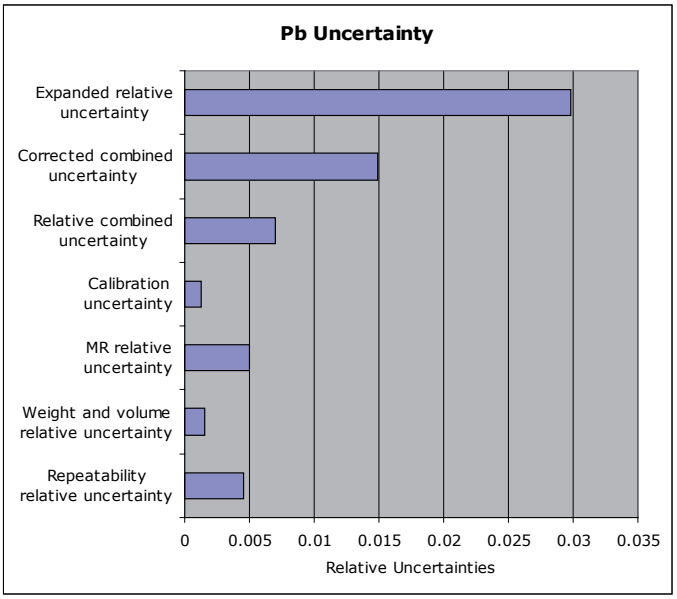
The uncertainty of Pb, Cd and Sb contents in the analyzed glazes has been calculated according to the procedure reported in the ARPA handbook [16,17,18,19].

Taking into account the previous formula, the different contributions to the uncertainty evaluated in this study are repeatability, weight, volume, reference material and calibration curve. In this case combined uncertainty is given by the square root of the sum of the single uncertainty raised to the second power while the corrected combined uncertainty keeps count of the number of replications run during the test for the determination of uncertainty (in this work 8) and the number of replicates in routine analysis (in normal condition 2).

The final relative expanded uncertainty is obtained with a coverage factor set to 2 when degrees of freedom are more than 10 while in the other cases the coverage factor is set equal to the value of Student's t for the level of confidence 95%.

The final results about the uncertainties calculated are reported in Graph 1÷7 and Table 4÷10.

Reference Material Multicomponent Glass – PbO (4.40± 0.13)%

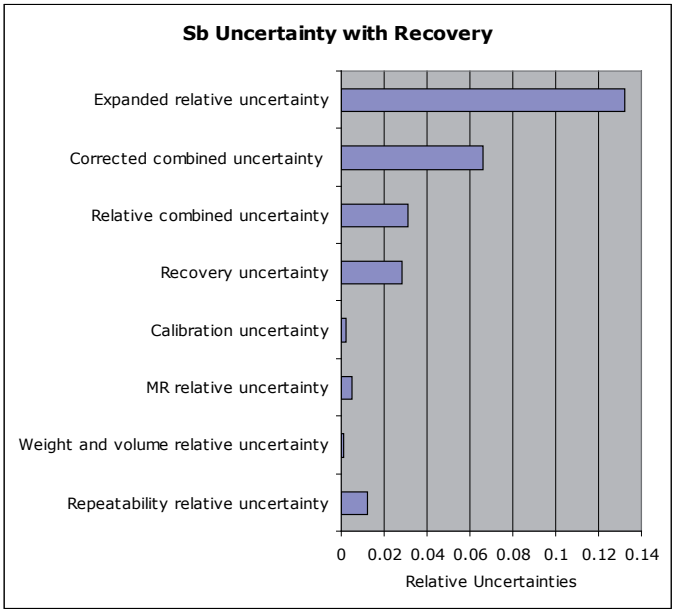


Graph 5. Multicomponent Glass-relative contributions to Pb uncertainty.

Repeatability relative uncertainty	Weight and volume relative uncertainty	MR relative uncertainty	Calibration uncertainty	Relative combined uncertainty	Corrected combined uncertainty	Expanded relative uncertainty	Expanded uncertainty %
0.004557	0.001561	0.004966	0.001268	0.007034	0.014921	0.029843	0.13131

Table 8. Multicomponent Glass–Pb uncertainty contributions.

Glaze C3 – Sb_2O_3 (0.88±0.12)%

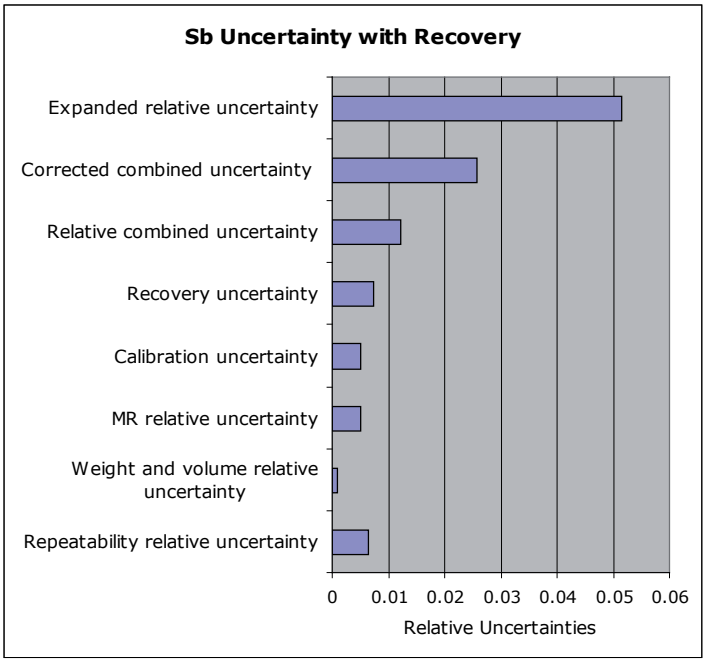


Graph 6. Glaze C3-relative contributions to Sb uncertainty.

Repeatability relative uncertainty	Weight and volume relative uncertainty	MR relative uncertainty	Calibration uncertainty	Recovery uncertainty	Relative combined uncertainty	Corrected combined uncertainty	Expanded relative uncertainty	Expanded uncertainty %
0.012108	0.000946	0.004967	0.002027	0.028141	0.031116	0.066007	0.132015	0.11617

Table 9. Glaze C3–Sb uncertainty contributions.

Glaze C1 – Sb_2O_3 (0.12±0.01)%



Graph 7. Glaze C1-relative contributions to Sb uncertainty.

Repeatability relative uncertainty	Weight and volume relative uncertainty	MR relative uncertainty	Calibration uncertainty	Recovery uncertainty	Relative combined uncertainty	Corrected combined uncertainty	Expanded relative uncertainty	Expanded uncertainty %
0.006494	0.000946	0.004967	0.005037	0.007360	0.012135	0.025743	0.051486	0.00618

Table 10. Glaze C3–Sb uncertainty contributions.

We consider that a proper value for uncertainty has to be lower than 10%, so among all the results obtained, the acceptable results are those indicated in the table 11:

Element	Ecolabel limit	Concentra-tion (%)	Uncertainty (%)	Relative Value (%)	Compliance
CdO	0.1	4.38	0.19	4.3	yes
		0.27	0.01	3.7	yes
PbO	0.5	4.40	0.13	3.0	yes
		0.70	0.06	8.6	yes
		1.50	0.28	18.7	no
Sb_2O_3	0.30	0.12	0.01	8.3	yes
		0.88	0.12	13.6	no

Table 11. comparison between Ecolabel limits and experimental data.

5. DISCUSSION AND CONCLUSIONS

According to the acceptable criteria it has to be underlined that Cd is conformable to 10% uncertainty requirements for both concentration contents (4.38 and 0.27%). Pb, instead, shows a higher uncertainty concerning 1.50% concentration. Uncertainty of 0.12% content about Sb is conformable, on the contrary the higher content shows an uncertainty out of range. Cd, Sb and Pb calculated uncertainties comply with the method demands because all the three elements shows uncertainties lower than 10% for the concentrations comparable to the Ecolabel limits (CdO limit 0.1% versus sample content 0.27%; PbO limit 0.5% versus sample content 0.70% and Sb_2O_3 limit 0.30% versus sample content 0.12%).

For the two cases where the compliance to the acceptance criterion is not fulfilled it will be possible to find the proper operating conditions which will lower uncertainty if time and cost consideration will be supported by such a degree of validation demand.

In any case the work done has achieved two goals:

1. A first evaluation of the ruggedness (or robustness) of this new method. "The robustness of an analytical procedure is a measure of its capacity to remain unaffected by small, but deliberate variations in method parameters and provides an indication of its reliability during normal usage". Two different type of materials has been investigated –a glass and 3 ceramic glazes.
2. For each element Pb, Cd and Sb uncertainty calculation has been run for a range of concentrations and not only for one value.

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